

## Seasonal variation of high-molecular-weight compounds in the water-soluble fraction of organic urban aerosols

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Received 23 February 2005; revised 24 August 2005; accepted 26 September 2005; published 10 December 2005.

[1] Aerosol samples were collected in Zurich, Switzerland, at an urban background site and were analyzed with size exclusion chromatography (SEC) and laser/desorption ionization mass spectrometry (LDI-MS) for water-soluble organic compounds with high molecular weight. Daily samples were collected during two campaigns in winter and summer, for 1 month each. The concentration of high-molecular-weight compounds (humic-like substances (HULIS)) was between 0.4 and 4  $\mu\text{g}/\text{m}^3$  in winter and summer. The most intense signals in the LDI-MS mass spectra were measured between  $m/z$  150 and 500, comparing well with the mode of the two main high mass peaks determined with SEC corresponding to masses between 200 and 600 Da. For the maximum molecular weight, however, different results were obtained by the two techniques: whereas a maximum molecular weight between 1300 and 3300 Da was found with SEC, hardly any peaks above  $m/z$  700 were measured with LDI-MS. During summer the maximum molecular weight of HULIS (determined with SEC) correlates positively with several parameters such as ozone and increased temperature indicative of enhanced atmospheric photo-oxidation. The HULIS concentration also correlates positively with the oxalic acid concentration in the particles. This suggests that HULIS are generated by secondary processes in summer. The lack of such correlations during winter suggests that other sources and processes might be important during colder seasons.

**Citation:** Samburova, V., S. Szidat, C. Hueglin, R. Fisseha, U. Baltensperger, R. Zenobi, and M. Kalberer (2005), Seasonal variation of high-molecular-weight compounds in the water-soluble fraction of organic urban aerosols, *J. Geophys. Res.*, 110, D23210, doi:10.1029/2005JD005910.

### 1. Introduction

[2] Although up to 50% of the total mass of ambient aerosol is organic material, only little is known about this aerosol fraction, and only 10–20% of the organic mass can be resolved on a molecular level. In recent years, high-molecular-weight compounds have received considerable attention as components of atmospheric organic aerosols and cloud water constituents. Several studies showed that these compounds have characteristics similar to those of humic acids, especially their UV and fluorescence spectra. They are therefore often named humic-like substances (HULIS) [e.g., Havers *et al.*, 1998; Zappoli *et al.*, 1999]. Size exclusion chromatography (SEC) was often used to separate this class of aerosol components from lower

molecular weight compounds [Zappoli *et al.*, 1999; Krivácsy *et al.*, 2000; Samburova *et al.*, 2005], and various detection methods were applied such as UV, IR, and fluorescence spectroscopy, as well as electrospray ionization mass spectrometry [Zappoli *et al.*, 1999; Krivácsy *et al.*, 2000; Kiss *et al.*, 2003].

[3] For quantitative statements most analytical techniques require standard compounds that are chemically or physically similar to the analytes. However, since the chemical properties of HULIS are still largely unknown, an absolute molecular weight determination or an exact concentration determination of these compounds is difficult to achieve with most analytical methods. Kiss *et al.* [2003] analyzed HULIS extracted from fog samples with electrospray ionization mass spectrometry and reported a maximum molecular weight around 500 Da. A comparison of SEC results with laser desorption/ionization mass spectrometry (LDI-MS) yields similar estimates for the molecular weight distribution of HULIS in aerosols collected at an urban background site [Samburova *et al.*, 2005]. Concentration estimates using Suwannee River Fulvic Acid (SRFA) as a standard showed that about 10% of the total organic carbon (OC) could be attributed to these high-molecular-weight compounds [Samburova *et al.*, 2005]. The sources and formation mechanisms of this aerosol fraction are still

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**Table 1.** Sampling Times, HULIS Concentrations (SRFA Equivalents), and Percentage of HULIS in Total Organic Carbon of Samples Collected at an Urban Background Site in Downtown Zurich, Switzerland, in Summer 2002 and Winter 2003

Sample Name	Summer Samples			Winter Samples			
	Sampling Time	HULIS Concentration, $\mu\text{g}/\text{m}^3$	HULIS/OC, %	Sample Name	Sampling Time	HULIS Concentration, $\mu\text{g}/\text{m}^3$	HULIS/OC, %
Day Samples							
D1S	13/14 Aug	0.42	9.6	D1W	18/19 Feb	3.31	24.4
D2S	15/16 Aug	0.51	11.7	D2W	20/21 Feb	3.87	20.8
D3S	17/18/19 Aug	0.60	12.2	D3W	22/23 Feb	2.90	17.4
D4S	21/22 Aug	0.64	30.6	D4W	24/25 Feb	2.70	20.8
D5S	23/24 Aug	0.67	10.9	D5W	26/27 Feb	1.99	18.5
D6S	25 Aug	1.44	23.1	D6W	1/2 Mar	0.67	16.1
D7S	27/28/29 Aug	0.46	12.9	D7W	3/4 Mar	0.72	17.5
D9S	3 Aug	0.60	17.7	D8W	5/6/7 Mar	0.54	9.8
D10S	5/6 Aug	0.64	11.1	D9W	8/9 Mar	0.40	18.3
D11S	7/8 Aug	0.44	11.5	D10W	10/11 Mar	0.61	11.9
Average day		0.64	15.1	D11W	12/13 Mar	0.56	18.9
				D12W	22/23 Mar	1.61	21.3
						1.66	18.0
Night Samples							
N1S	13/14 Aug	0.44	12.5	N1W	17/18 Feb	2.09	19.9
N2S	14/15 Aug	0.43	9.1	N2W	19/20 Feb	2.53	17.1
N3S	17/18/19 Aug	0.47	8.3	N3W	21/22 Feb	2.24	13.6
N4S	20/24 Aug	0.41	10.2	N4W	23/24 Feb	2.45	... <sup>a</sup>
N5S	22/23 Aug	0.59	8.6	N5W	25/26 Feb	1.64	... <sup>a</sup>
N6S	24/25 Aug	0.78	10.9	N6W	28 Feb/1 Mar	1.01	... <sup>a</sup>
N7S	26/27/28 Aug	0.37	8.7	N7W	2/3 Mar	0.43	... <sup>a</sup>
N9S	2/3 Aug	0.37	6.0	N8W	4/5 Mar	0.66	13.6
N10	4/5 Aug	0.55	7.5	N9W	6/7 Mar	0.47	13.6
N11	6/7 Aug	0.64	9.6	N10W	8/9 Mar	0.42	12.2
Average night				N11W	10/11 Mar	0.63	17.4
				N12W	12/13 Mar	0.35	28.1
				N13W	22/23 Mar	1.20	... <sup>a</sup>
Average night		0.51	9.14			1.24	15.4
Day/night of average		1.25	1.65			1.34	1.17

<sup>a</sup>OC not measured.

highly speculative. *Facchini et al.* [1999] found increased levels of levoglucosan with increased HULIS concentrations suggesting that biomass burning is a significant source of these compounds.

[4] High-molecular-weight compounds were also found recently in laboratory experiments. Mass spectrometric analysis of secondary organic aerosols formed from aromatic and terpene precursors showed oligomer structures up to about  $m/z$  900 [Kalberer *et al.*, 2004; Tolocka *et al.*, 2004; Baltensperger *et al.*, 2005]. The formation mechanisms of these compounds, which make up to 50% of the particle mass, is not well understood but oligomerization of small volatile carbonyls forming acetals was suggested as one possible formation mechanism [Kalberer *et al.*, 2004; Tolocka *et al.*, 2004; Iinuma *et al.*, 2004; Jang *et al.*, 2002].

[5] In this paper we present measurements of HULIS concentrations and their molecular weight distribution from aerosol samples collected at an urban background site in Zurich, Switzerland, and their seasonal variations during two campaigns, one in summer 2002 and one in winter 2003.

## 2. Experiment

### 2.1. Sampling

[6] Atmospheric aerosol particles were sampled in downtown Zurich, Switzerland, at an urban background station of the Swiss National Air Pollution Monitoring Network (NABEL) in August 2002 and in February/March 2003 (Table 1). The site is situated in a park-like courtyard in the city centre close to the main railway station. It is surrounded in the immediate vicinity by roads with low traffic as well as apartment buildings, small companies, and shops [Empa, 2000].

[7] Particles smaller than 10  $\mu\text{m}$  in aerodynamic diameter (PM<sub>10</sub>) were collected on prebaked quartz fiber filters (150 mm diameter) with a high-volume sampling system at a flow rate of 500 l/min (Model DA 80, Digtel AG, Switzerland). Daytime and nighttime samples were collected during 12 hours for one to three consecutive days and nights, respectively, resulting in a total sampling time of 12–36 hours. Sampling for the daytime filters started between 7:00 and 8:00 and ended between 19:00 and 20:00. Night samples were collected from 19:00 or 20:00 to 7:00 or 8:00 (Table 1). No denuders were used during sampling so that heterogeneous reactions of gaseous oxidants with aerosol components deposited on the filter cannot be excluded, which might result in positive or negative sampling artifacts for the HULIS determination. However, no correlation of the HULIS concentration with potential oxidants such as ozone or NO<sub>2</sub> concentration was observed (although a positive correlation of ozone and the maximum molecular weight of HULIS was observed, see below). In addition to the daily samples analyzed in this study we collected samples for five consecutive days during the summer campaign. The HULIS concentration in these samples (0.3–0.5  $\mu\text{g}/\text{m}^3$ ) is consistent with the concentrations found in the daily samples (see Table 1 and Samburova *et al.* [2005]). If heterogeneous reactions of HULIS with oxidants on the filter were important one would expect that longer sampling times result in HULIS concentrations that differ

from short sampling times. In addition, several experiments during both campaigns were performed with two filters behind each other also to assess possible sampling artifacts. It is known that during sampling, volatile gaseous components can adsorb to filters resulting in an overestimation of the aerosol phase. Less than 3% of the total HULIS mass was found on the back filter extract measured by SEC-UV. Because it is unlikely that high-molecular-weight compounds are present in the gas phase, this small mass fraction found on the back filter is most probably due to heterogeneous reactions of volatile organic gaseous compounds with oxidants on the filter or due to small volatile compounds with substantially different elution characteristics than PMA (used for the size calibration, see below) so that they elute in the defined retention time window of HULIS. These test experiments show that heterogeneous formation (or loss) of HULIS on the filter is of minor importance, however, further studies will have to look at this aspect in more detail.

[8] After sampling, filters were wrapped into aluminum foils and stored in polyethylene bags at  $-28^\circ\text{C}$  until analysis.

[9] The sample work-up procedure has been described in detail elsewhere [Samburova *et al.*, 2005]. Shortly, ten 15-mm diameter circular cuts of each filter were extracted with Milli-Q water (18 M $\Omega$ ·cm). Filters were soaked in the solvent during 2 hrs. Samples were then centrifuged to separate solid particles and the filter material from the supernatant solution. Extractions of the filters in apolar solvents (i.e., tetrahydrofuran and toluene) yielded no detectable signal in SEC-UV and LDI-MS analysis, showing the polar properties of atmospheric HULIS.

### 2.2. SEC Analysis

[10] Size exclusion chromatographic (SEC) measurements were performed using a Waters Ultrahydrogel 120 column (300 mm  $\times$  7.8 mm, hydroxylated polymethacrylate stationary phase), and a HPLC system from Shimadzu with a UV diode array detector (190–800 nm). An aqueous buffer solution (0.3M NaCl, 0.03M NH<sub>4</sub>Cl, pH 10–11 adjusted with NH<sub>4</sub>OH) at a flow rate of 1 ml/min was used as eluent [Krivácsy *et al.*, 2000]. Polymethacrylic acid sodium salt standards (PMA, Fluka, Switzerland) were used for size calibration of HULIS. Size calibration of SEC columns requires that the chemical properties of the analyte (in our case HULIS) and the calibration compound are similar. Because the chemical properties of HULIS are not known, several standards of different polarities were compared for a molecular weight calibration, i.e., nonionogenic polyethylene glycols (PEG), ionogenic polymethacrylic acids (PMA) and dicarboxylic acids (succinic, adipic and acelaic acid). PEG and PMA resulted in largely different calibration curves, whereas the dicarboxylic acids fit well into the PMA calibration because of their similar chemical structure. A size calibration curve was established using the PMA standards and the dicarboxylic acids as standards.

[11] HULIS are rather polar compounds, with multiple acid functionalities as indicated by the extraction results with apolar solvents and consistent with literature data [Zappoli *et al.*, 1999]. Thus it is expected that they are separated on the column similar to the polyacid PMA. Using the PMA calibration curve, the mode of the two most intense peaks in the HULIS chromatograms between

6.4–6.6 min and 6.8–7.0 min correspond to molecular weights of about 450–600 Da and 200–300 Da, respectively. LDI-MS measurements (see below and Figure 4) show the most intense peaks (not to be confused with the highest measured  $m/z$  peaks) between 150 and 500 Da, supporting PMA as size calibration compound [Samburova *et al.*, 2005].

[12] SRFA (International Humic Substances Society, IHSS) was used as quantification standard in the SEC-UV experiments [Samburova *et al.*, 2005]. SRFA was chosen as calibration compound for a quantitative HULIS determination because it is widely used and chemically well characterized [e.g., Noyes and Leenheer, 1989]. In addition, the molecular size distribution of SRFA is <1000 Da as determined by various methods, among them LDI-MS and MALDI-MS [Novotny and Rice, 1995; Brown and Rice, 2000; Leenheer *et al.*, 2001; Kujawinski *et al.*, 2002]. The same molecular size range is expected for HULIS [Kiss *et al.*, 2003].

[13] Using SRFA as surrogate quantification standard for HULIS may cause systematic errors, which are described in detail in Samburova *et al.* [2005]. Shortly, the following aspects have to be considered.

[14] 1. Water soluble inorganic compounds (mostly nitrate and sulfate), which are present in the aerosol sample and which are absorbing at 240 nm (the wavelength used here for quantification) have to be separated from the HULIS. This was achieved for nitrate by the chromatographic method described above. Sulfate, also an abundant inorganic aerosol component is eluting within the HULIS retention time window, however, absorption at 240 nm is negligible for the concentrations present in the aerosol samples.

[15] 2. The extinction coefficient of SRFA and HULIS might be different in the retention time window of HULIS (<6.8 min). Thus the quantitative results obtained are considered as “SRFA equivalent” concentrations.

### 2.3. LDI-MS Analysis

[16] In addition, laser desorption/ionization mass spectrometry (LDI-MS) was used to determine the molecular weight distribution of the compounds present in the urban atmospheric aerosol and for comparison with the SEC measurements. The LDI-MS experiments were performed with a time-of-flight mass spectrometer (Axima-CFR, Kratos/Shimadzu, Manchester, UK). 50  $\mu$ l of the aqueous extract was directly added to the target stainless steel plate and the water was evaporated in a dessicator. The LDI-MS measurement was performed without further treatment using laser powers between 20 and 25  $\mu$ J/pulse as described in more detail by Samburova *et al.* [2005]. Several experiments were performed to assure that measurement artifacts (especially fragmentation of larger molecules) in LDI-MS did not significantly influence the determination of the molecular weight distribution. Measurements at lower laser power did not result in a shift to higher masses, but only to lower signal intensities, which is an indication that fragmentation of larger compounds is likely not a serious problem. In addition, no significant post source fragmentation for several investigated masses up to  $m/z$  430 was observed. To further check the possibility whether fragmentation during the measurement would significantly cause an

apparent shift to smaller masses, the addition of various organic and inorganic matrices to the sample was studied because matrix addition often results in a softer ionization. No shift of the overall mass spectrum to larger masses could be observed after addition of matrix. Instead the complexity of the spectra increased because of matrix peaks and matrix-analyte adducts. The fact that matrix addition did not result in significantly higher signal intensities nor in a shift of the spectra to higher masses might be due to compounds present in the complex aerosol sample that act as matrices by absorbing the desorption laser light and assuring efficient ionization. For a more detailed discussion on possible LDI-MS artifacts see Samburova *et al.* [2005].

[17] Total organic carbon was determined for all samples by a custom-built two-step combustion method as described in detail by Szidat *et al.* [2004]. Several organic acids in the particles were determined during the same sampling campaigns with an online wet effluent diffusion denuder/aerosol collector ion chromatograph as described in detail by Fisseha *et al.* [2004].

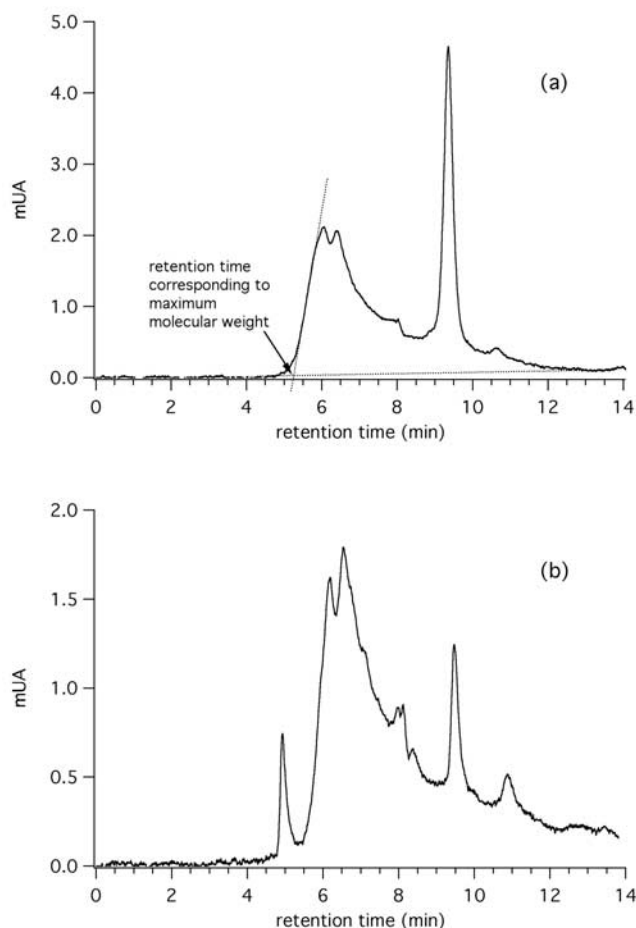
## 3. Results and Discussion

### 3.1. Molecular Weight Determination of HULIS

[18] The molecular weight distribution of the water-soluble high-molecular-weight compounds in atmospheric aerosols was determined by two different methods, SEC-UV and LDI-MS. SEC analyses of all filter samples yielded very similar chromatograms with peaks at retention times between 5.0 min and 12.0 min as seen in the two typical chromatograms in Figure 1. Compounds eluting with retention times shorter than 6.8 min have a molecular weight >300 Da (using PMA for size calibration) and are defined here as water soluble high-molecular-weight compounds (HULIS). Comparison of the SEC and LDI-MS results showed that PMA (polymethacrylic acid) and dicarboxylic acids are suitable molecular weight standards for HULIS as described above and by Samburova *et al.* [2005]. The retention time of the two main peaks in the high mass region at about 6.5 and 6.9 min is remarkably stable for all samples ( $\pm 0.1$  min). The first of the two peaks corresponds to masses between 450–600 Da with a slight shift toward shorter retention times (i.e., higher masses) in winter and the second peak corresponds to masses between 200 and 300 Da.

[19] The maximum molecular weight of HULIS was determined by fitting the onset of the first peak at about 6.5 min [Hunt and Holding, 1989], a usual technique in polymer analysis when molecular weight distributions are determined (tangential fit, see Figure 1a). The maximum molecular weight of HULIS in winter (Figure 2a) is found to be significantly higher (between 2200 and 3300 Da) than in summer (1300 and 2400 Da, Figure 2b). Statistical errors in the molecular weight determination with SEC are  $\leq \pm 0.03$  min (equivalent to errors  $\leq \pm 250$  Da, see Figures 2 and 3). Systematic errors are mostly due to the choice of the calibration compound (in our case PMA) and likely larger than the statistical errors. As described above and by Samburova *et al.* [2005], we conclude that the polyacid PMA is a reasonable calibration compounds for atmospheric HULIS.





**Figure 1.** Size-exclusion chromatograms of the water extract of atmospheric aerosols collected (a) in winter (samples number D1W) and (b) in summer (sample number N2S) at an urban background site in Zurich, Switzerland. For explanation of tangential fit, see text.

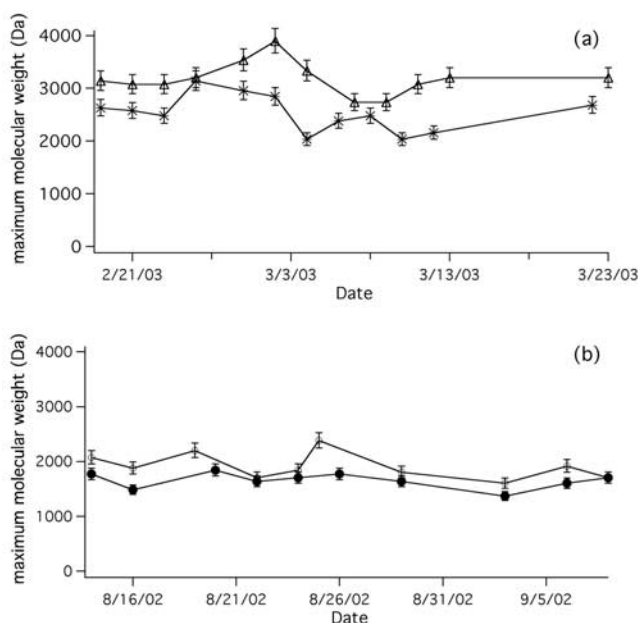
[20] For the summer samples, a clear positive correlation of the maximum molecular weight with temperature is visible, whereas such a trend is not seen during winter (Figure 3a). In summer, the maximum molecular weight also correlates positively with ozone concentrations (Figure 3b). These positive correlations (statistically significant on a 95% confidence level, see Figures 3a and 3b) suggest that in summer polymerization is favored by increased photochemical activity. The sources of the gaseous precursors remain to be elucidated. In winter these correlations are not found indicating that other sources and processes are mainly involved in the HULIS formation in winter (see below).

[21] Peaks at retention times shorter than 5.4 min include compounds with a molecular weight higher than the exclusion limit of the column (ca. 4000 Da). Only in the summer samples (in 40% of the day and 70% of the night samples) a peak at 5.2–5.4 min was observed (Figure 1b), whereas such a peak was never measured during winter (Figure 1a). The occurrence of this small peak in the summer samples with an estimated molecular weight  $>4000$  Da may be explained by the higher abundance of primary biogenic emissions in summer such as plant debris, pollen or spores

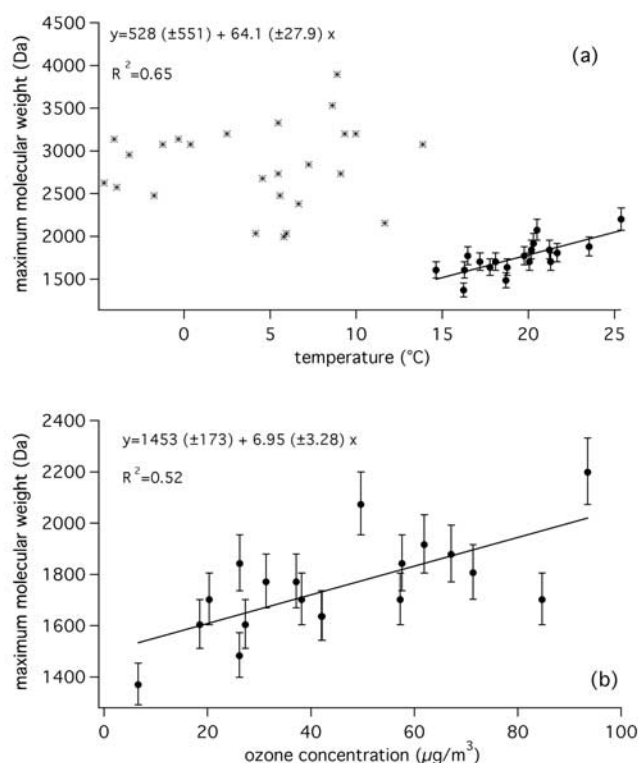
containing cellulose, starch, or other large molecules such as proteins or membrane fragments. In addition to the peaks in the high-molecular-weight range ( $>300$  Da) most chromatograms show a distinct peak between 9 and 10 min retention time (Figures 1a and 1b). Nitrate is eluting at this retention time so that part of the signal intensity of the peak at about 10 min is due to nitrate. This peak is most prominent during winter, whereas only a small peak is seen in the summer night samples. In the summer day samples this peak is completely absent consistent with the strong temperature-dependent volatility of ammonium nitrate in aerosols as also measured by Fisseha *et al.* [2005] during the same sampling campaigns. In addition, as described in detail by Samburova *et al.* [2005], organic compounds eluting so late in the chromatogram are attributed to low molecular weight compounds with relatively nonpolar properties. Thus this peak might also partly be due to smaller semivolatile organic compounds.

[22] The general structure of the chromatograms compares well with chromatograms of HULIS from fog samples collected in the Po valley (Italy), which also exhibit broad high-molecular-weight peaks and a single, intense peak at longer retention times [Krivácsy *et al.*, 2000].

[23] LDI-MS was used as an additional method for the molecular weight distribution of water-soluble organic compounds. The peaks with highest intensity were detected between  $m/z$  150–500 (Figure 4). This corresponds well with the mode of the two most intense high-molecular-weight peaks of the SEC measurements at about 6.5 and 6.9 min corresponding to masses of about 200–600 Da. In LDI-MS there are hardly any peaks found above  $m/z$  700,



**Figure 2.** Maximum molecular weight of HULIS in (a) winter (triangles indicate day, and asterisks indicate night) and (b) summer (open circles indicate day, and solid circles indicate night). The molecular weight of HULIS was determined with SEC-UV using PMA as size calibration surrogate standard. Shown error bars represent statistical errors of the SEC determination.



**Figure 3.** Correlation between maximum molecular weight and (a) temperature (solid circles indicate summer, and asterisks winter) and (b) ozone (summer data). The linear fit in Figure 3a includes only the summer data. The correlation coefficient and the equation of the linear fits are also shown. The 95% confidence intervals for the estimated intercept and slope are given in parentheses. Shown error bars represent statistical errors of the SEC determination.

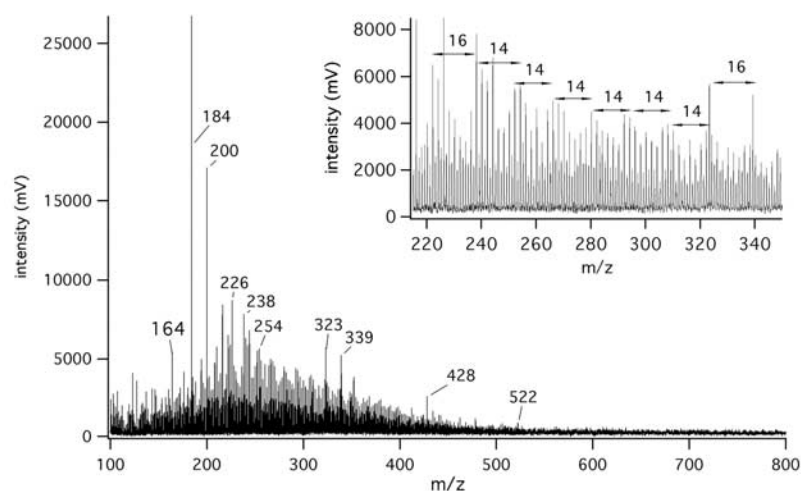
although in SEC higher masses were determined for all samples. Several reasons might explain this significant discrepancy of the maximum molecular weight determined with the two methods. First, ionization efficiencies of these large

molecules could be so low that they are not detected with LDI-MS. Second, these compounds might fragment during the desorption or ionization process to products with masses lower than  $m/z$  700. However, as described above, fragmentation was not found to be a dominant process. Third, one has to keep in mind that the present size calibration for SEC was performed with PMA, assuming that HULIS have chromatographic characteristics similar to those of PMA. Thus these earliest eluting compounds might partially be due to aerosol components with elution characteristics substantially different from PMA. Despite the discrepancies of the two methods at the high end of the molecular size distribution they agree very well for the peaks with highest intensity.

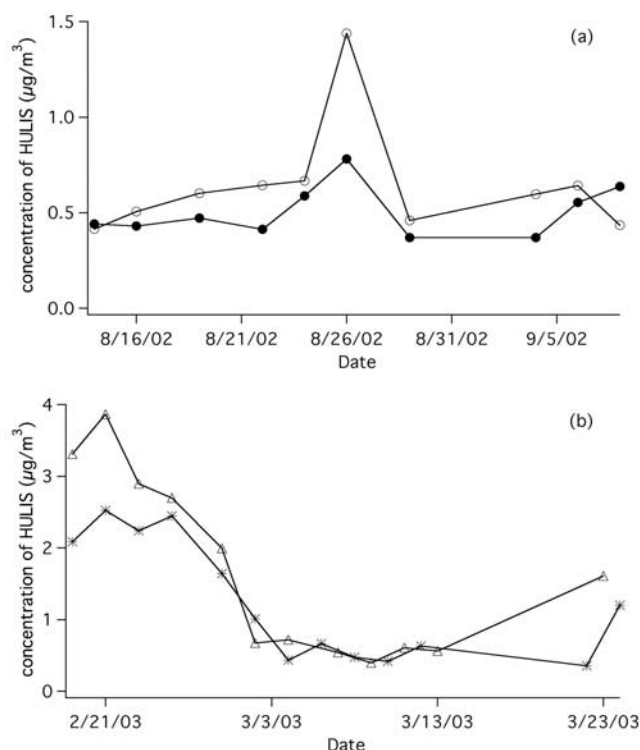
[24] These LDI-MS spectra are in agreement with the results of other authors [Kiss *et al.*, 2003; Krivácsy *et al.*, 2000] who found similar molecular weight distributions for HULIS in aerosol and fog water samples analyzed with electrospray ionization – mass spectrometry. Spectra of all samples show peaks with distinct mass differences of  $\Delta m$  14 and 16 (see insert in Figure 4), which can be interpreted as differences due to additional  $\text{CH}_2$  groups and additional oxygen atoms, respectively, incorporated into the molecules. Similar mass patterns were found in organic aerosols from smog chamber experiments [Kalberer *et al.*, 2004; Tolocka *et al.*, 2004].

### 3.2. Determination of the HULIS Concentration

[25] Figures 5a and 5b show the SRFA equivalent concentration of HULIS during daytime and nighttime, for the summer and winter campaign, respectively. The HULIS concentrations were determined using SRFA as a standard for UV absorption. The concentration of HULIS between 17 and 26 February 2003 (samples D1W-D5W, N1W-N5W) was up to ten times higher than in the other samples. This is due to a strong inversion layer present over Zurich during this time period, when unusually high concentrations of daily  $\text{PM}_{10}$  up to  $130 \mu\text{g}/\text{m}^3$  were observed. Later during the winter campaign as well as during summer, the HULIS concentrations were considerably lower (between 0.4 and  $1.6 \mu\text{g}/\text{m}^3$ , see Table 1 and Figure 5). Average daytime



**Figure 4.** LDI-MS spectrum of HULIS between  $m/z$  100 and 800. Insert shows the mass spectrum of the same sample from  $m/z$  210 to 350 illustrating the repetitive mass pattern of  $\Delta m$  14 and  $\Delta m$  16.



**Figure 5.** Concentrations of HULIS in (a) summer (open circles indicate day, and solid circles indicate night) and (b) winter (triangles indicate day, and asterisks indicate night).

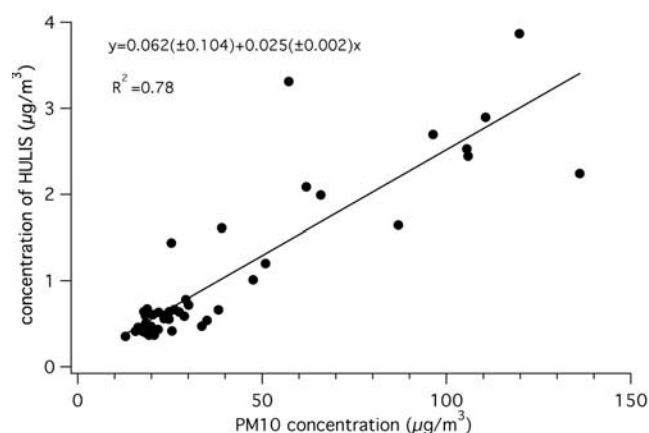
values were about 25% and 35% higher than the nighttime values for the summer and winter campaign, respectively.

[26] The concentration of HULIS correlates significantly with the PM<sub>10</sub> concentration as shown in Figure 6. On average, the HULIS concentration is about 2.5% of the PM<sub>10</sub> mass and 6–31% of the total organic carbon (OC) (Table 1). The total organic mass is often estimated by multiplying the organic carbon mass with a factor. In this study, a factor of 1.9 was applied, which agrees with the findings of Krivácsy *et al.* [2001] for the Jungfraujoch aerosol as well as of Kalberer *et al.* [2004] for SOA formed in smog chamber experiments. Turpin and Lim [2001] give conversion factors, of  $1.6 \pm 0.2$  for urban aerosols and  $2.1 \pm 0.2$  for aged (nonurban aerosols). Using a conversion factor of 1.9 about 3–16% of the total organic aerosol mass consists of HULIS. The HULIS fraction in total OC correlates positively with the maximum molecular weight (Figure 7a). With a higher HULIS mass fraction in the organic aerosol reactions of two smaller oligomers with each other might be more frequent, resulting in larger molecules. In addition, oxalic acid, a compound largely formed in secondary processes in the atmosphere [e.g., Limbeck and Puxbaum, 1999], also correlates positively with the HULIS concentration (Figure 7b). Oxalic acid was independently determined with an online wet effluent denuder/aerosol collector ion chromatograph at the same sampling site and time (for instrument and method description see Fisseha *et al.* [2004]). This again suggests that higher photochemical activity promotes a higher concentration of HULIS in the particles.

[27] Although the HULIS concentrations in winter are comparable to the summer concentrations (see Table 1), secondary formation processes are likely less important in winter. S. Szidat *et al.* (unpublished manuscript, 2005) analyzed the same filters investigated here for  $^{14}\text{C}$  in various carbonaceous particle fractions and concluded that in winter about 80% of the total water soluble OC was from nonfossil fuel sources and about 38% of the total OC was attributed to biomass burning. Thus, in winter a substantial fraction of the HULIS might not be due to secondary atmospheric oxidation processes but due to primary emissions from wood combustion.

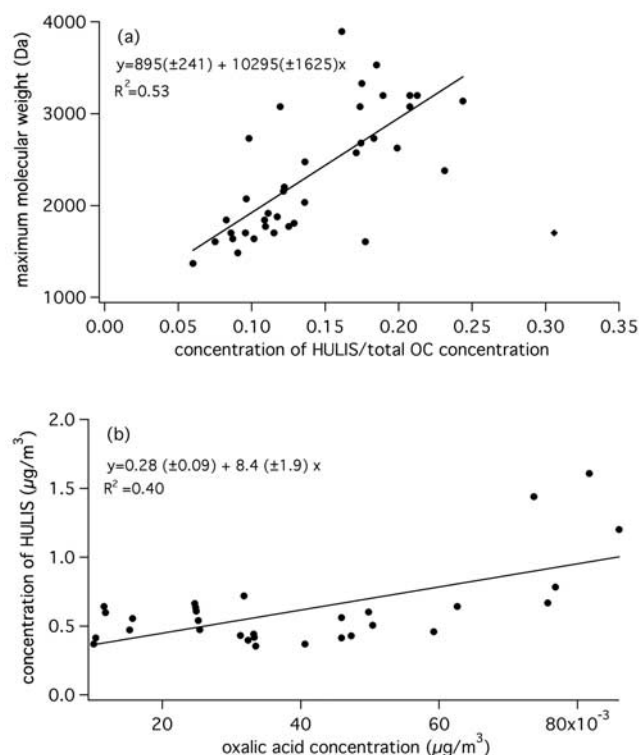
[28] Alternative sources and routes for formation of HULIS have been suggested in the literature: in particular, on the basis of both laboratory experiments and field studies done during winter, Hoffer *et al.* [2004] and Facchini *et al.* [1999] proposed that HULIS might be formed from precursors due to biomass burning. A subset of the filters collected for our study was analyzed for levoglucosan, a tracer for wood combustion (S. Szidat *et al.*, unpublished manuscript, 2005). No statistically significant correlation between the concentration of levoglucosan and that of HULIS was found. However, it must be emphasized that only four samples of the winter campaign, the season with highest wood burning activity, could be analyzed for levoglucosan. Thus further studies are necessary to obtain a more detailed source apportionment of HULIS.

[29] Several authors [Limbeck *et al.*, 2003; Iinuma *et al.*, 2004; Tolocka *et al.*, 2004; Baltensperger *et al.*, 2005] demonstrated that high-molecular-weight compounds are present in SOA formed from isoprene and terpenes, the main biogenic SOA precursors, and Kalberer *et al.* [2004] showed that SOA from aromatic compounds (i.e., anthropogenic precursors) contains significant amounts of high-molecular-weight compounds. Decesari *et al.* [2002] suggested that oxidation of soot (emitted predominantly by anthropogenic activities) with ozone yields water-soluble compounds with characteristics similar to HULIS found in ambient particles. Further work is needed to assess the



**Figure 6.** Correlation between the HULIS concentration and PM<sub>10</sub>. The correlation coefficient and the equation of the linear fits are also shown. The 95% confidence intervals for the estimated intercept and slope are given in parentheses.





**Figure 7.** Correlations between HULIS concentration and maximum molecular weight of (a) HULIS (data point at HULIS/total OC = 0.3 is not included in the regression) and (b) oxalic acid. The correlation coefficient and the equation of the linear fits are also shown. The 95% confidence intervals for the estimated intercept and slope are given in parentheses.

importance of the various sources for atmospheric HULIS as a function of season or emission characteristics.

#### 4. Conclusions

[30] Water-soluble high-molecular-weight compounds (HULIS) were analyzed in atmospheric aerosols (PM<sub>10</sub>), which were collected at an urban background site in Zurich, Switzerland, in winter and summer for 1 month each. The molecular weight distribution of the HULIS was determined with SEC-UV and LDI-MS. The two major peaks in the high-molecular-weight range correspond to about 200–600 Da as determined with SEC-UV comparing well with LDI-MS results, where the most intensive peaks were measured between *m/z* 150 and 500. The maximum molecular weight as determined with SEC-UV was significantly higher in winter than in summer and showed for summer positive correlations with temperature and ozone suggesting secondary, photochemically driven formation processes of HULIS. This is also supported by the positive correlation of the HULIS concentration with oxalic acid.

[31] In view of the measurements presented here and of literature data, it can be concluded that precursors emitted into the atmosphere from a variety of sources are contributing to high-molecular-weight compounds in organic aerosols. During warmer periods it seems that generally enhanced photochemical activity increases the HULIS frac-

tion in total OC, suggesting that secondary formation processes are important. In winter, with increased wood burning activities in Europe, a contribution of biomass burning to HULIS seems probable.

[32] **Acknowledgments.** We thank the Swiss Agency for Environment, Forests and Landscape (SAEFL) for providing NABEL data. The support of the Swiss National Science Foundation (grants 2169-061393.00/2 and 200020-103605/1) and the Swiss Bundesamt für Bildung und Wissenschaft (EC project ACCENT, 03.0430-1; EU GOCE-CT-2004-505337) is greatly acknowledged. We thank Anne Kasper-Giebl, TU Vienna, for the levoglucosan measurements.

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